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(54) REMOVAL OF ARSENIC FROM WATER

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ABSTRACT

A process and apparatus for removing arsenic from water intended for drinking purposes in which the water is passed through a bed or column of a porous support material having impregnated thereon a substantially water insoluble ferric compound. Preferably the ferric compound is ferric hydroxide, which is produced in situ on the support material, and the treatment is carried out at a pH of 4-8.3. Optimum removal of arsenic occurs at pH 4.4.

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This invention relates to the purification of water and more particularly to the removal of arsenic from drinking water.

Certain sources of drinking water have, in certain geographical areas, been found to be contaminated with arsenic in amounts which could be injurious to life and health if the water is consumed by an individual over a long period. Such contamination is believed due to a natural leaching action from arsenical rocks and strata through which the water percolates. As is well known, arsenic is a cumulative poison in the body, that is it is not eliminated by normal body functions, and hence it tends to accumulate until it reaches a sufficient level to cause illness or even death. It is, therefore important that drinking water sources should be as free as possible of arsenical ions. The Canadian Government publication entitled "Public Health - A Handbook and Objectives", published in 1968, sets a series of Canadian Drinking Water Standards which specify 0.05 ppm maximum for arsenic in safe drinking water. Certain wells are known to contain 3.8 ppm and even more arsenic and it is clear that water from such wells must be treated before it is safe for human consumption. Iron sulfides, ion exchangers and activated charcoal have been used to remove arsenic from water but are not entirely satisfactory for reasons of cost, contamination by introduction of other ions or foreign matter, and difficulty of achieving contact between the arsenical water and the removal agent.

Arsenic in well water is believed to be present primarily as arsenate, and also as arsenite and a consideration of arsenate salts, particularly of Group II metals such as Ba, Sr, Ca and Mg, shows that arsenates generally decrease in solubility with a decrease in size of the cation. Ferric ions are, therefore, particularly suitable for removing arsenic from drinking water.

An object of the present invention is, therefore to provide a method for removing arsenic from drinking water by reaction of arsenic, gen-

erally in the form of arsenate, with ferric ions, preferably in the form of a substantially water insoluble ferric compound such as ferric hydroxide.

Another object of this invention is to provide an apparatus for the removal of arsenic from drinking water which is suitable for domestic use.

Thus, by one aspect of this invention there is provided a process for treating arsenic-containing water intended for drinking purposes comprising adjusting pH of said arsenic-containing water to the range 4-8.3, and treating said water with ferric ions to precipitate ferric arsenate therefrom and thus produce drinking water containing below 0.05 ppm arsenic.

By another aspect of this invention there is provided an apparatus for use in treatment of water for drinking purposes, comprising means containing a bed of a porous support material having impregnated thereon ferric hydroxide.

By yet another aspect of this invention there is provided a water treatment system for removing arsenic from water intended for drinking purposes comprising:

(a) water supply means;

(b) container means for attachment to said water supply means; and

(c) porous support material in said container means having impregnated thereon ferric hydroxide.

The invention will be described hereinafter in more detail with reference to the accompanying drawings in which:-

Figure 1 is a sketch of a water treatment system employing the concepts of the present invention; and

Figure 2 is a cross sectional view of a cartridge filter according to the present invention.

As noted hereinabove, arsenates decrease in solubility with a decrease in size of the cation and it can be shown quite readily that ferric ion forms an arsenate which has a solubility product of $10^{-20.24}$. Ferric hydroxide is a relatively non-hazardous material and is sub-

stantially insoluble in water so that it is highly suitable as a means of introducing ferric ions. Further, ferric hydroxide has the advantage of removing arsenic without introducing foreign matter into the water, i.e. the removal of arsenic by means of ferric hydroxide adds more water, as a product of the reaction, to the water.

$$Fe(OH)_3 + H_3AsO_4 \longrightarrow FeAsO_4 + 3H_2O$$

or: $$Fe^{+3} + 3H_2AsO_4^{-1} = Fe(H_2AsO_4)_3$$

followed by: $$Fe(H_2AsO_4)_3 = Fe(AsO_3)_3 + 3H_2O$$

Arsenate in acidic water hydrolyses to form the ions hydrogen arsenate and dihydrogen arsenate. A consideration of the dissociation constants of these ions, the solubility products of ferric arsenate and ferric hydroxide indicates that the removal of arsenic from drinking water should take place at a pH in the range 4-8.3 and that the optimum pH is about 4.4. Having determined that ferric ion is a particularly efficacious ion for the removal of arsenic from drinking water, there remains the problem of introducing ferric ions to a water purification system. It has been found that this problem may be overcome by carrying the ferric ions, preferably in the form of ferric hydroxide, on a porous, finely divided inorganic, support material, such as montmorillonite, scheelite, kieselguhr, fullers earth, vermicullite, diatomite, alumina or the like. Molecular sieves may also be employed as the support material but are expensive. The support material, generally in the size range 50-60 mesh, can then be contained in a cartridge for attachment to a domestic drinking water supply. Such cartridges generally containing sterilizing, deodorizing and clarification agents are, of course, well known in the art. It has been found preferable to generate the ferric hydroxide in situ on the support material, the method to be employed depending, at least in part, upon the specific support material employed. It is known, for example, that montmorillonite contains 3-4% of Fe and additional Fe may not be required. In general, however, the support material is impregnated with an aqueous solution of a water soluble salt, such as ferric chloride, ferric nitrate or ferrous sulphate, and the ferric ion is precipitated by the addition of sufficient

base such as alkali or alkaline earth metal hydroxides or ammonium hydroxide to increase the pH sufficiently to form ferric hydroxide. The resulting $Fe(OH)_3$ impregnated porous support material is then washed with water to remove excess reagent and can then be loaded into a filter bed or cartridge in known manner.

In Figure 1 there is shown, diagrammatically a subterranean well 1 from which water is pumped via pump 2 to a storage tank 3. Tank 3 may, of course, be of the gravity or pressure type and is normally connected to a distribution system 4. One arm 5 of the distribution system is provided with a suitable coupling for connection of the inlet side 11 (Figure 2) of a cartridge filter 6 of the present invention. Outlet side 12 of cartridge 6 is connected to a faucet 7 which provides drinking water. As shown more clearly in Figure 2 the impregnated porous support material 8 is retained in cartridge 6 by means of mesh screens 9 and 10 at the inlet and outlet ends respectively. Inlet and outlet ends 11 and 12 are provided with any suitable quick coupling devices such as captive cap couplings 13 and 14 respectively to facilitate removal and exchange of the cartridge 6.

In operation the pH of the water in the system is measured, at any suitable point, for example in tank 3, and adjusted as necessary by the addition of an acid or alkali to ensure that the pH is within the normally operative range 4-8.3 and preferably at about 4.4. It will be appreciated that the present invention may be employed in both municipal and private water treatment systems and is particularly suitable for small domestic systems where it is unlikely that sophisticated laboratory facilities will be found. Measurement of pH can, however, be carried out quickly and inexpensively by unskilled personnel using any of the known colorimetric methods readily available on the market.

<u>Example 1</u>

100g of 30-40 Mesh molecular sieve material 5A by Fisher

Scientific Company was impregnated with 4.6g of Fe^{+++} as $Fe(OH)_3$. The impregnated molecular sieve was then formed into a column 15.5" long and 1" diameter. 6810 mls of water with a pH of 4.7 and containing 3.8 ppm arsenic was passed through the column at a flow rate of 30 ml/min. The effluent was found to contain 0.042 ppm arsenic and 0.3 ppm Fe which is well below the recommended safe limits of 0.05 ppm As and 0.3 ppm Fe.

Example 2

80 g of 30-80 mesh diatomite containing 0.97% Fe^{+++} as $Fe(OH)_3$ was loaded into a column 12" long and 1" diameter. 4546 mls of water with a pH of 3.9 and containing 0.59 ppm arsenic was passed through the column at a flow rate of 100 ml/min. The effluent was found to contain less than 0.03 ppm arsenic, which is well below the recommended safe limit for drinking water.

As will be appreciated molecular sieves are relatively expensive and not therefore economically feasible for use in domestic water systems. Other support materials such as vermicullite and diatomite are, however, very much cheaper and, as indicated in Example 2, equally effective as a support material, so that it is anticipated that filter cartridges containing $Fe(OH)_3$ impregnated support materials will be available at acceptable commercial cost.

As previously indicated it is contemplated that cartridges of the present invention will be provided for domestic use and therefore no provision for regeneration of the cartridges has been made for safety reasons. It is contemplated that, depending on water throughput, a cartridge will be of sufficient size to have a useful life of 3-5 years and will normally be discarded after say 1 1/2 - 2 1/2 years. It is

of course, important that the cartridge does not reach saturation before discard and hence the relatively large safety factor to be allowed. The discarded cartridges will obviously contain a relatively large amount of arsenic and disposal thereof will require considerable care and attention. Municipal and industrial users may, of course, regenerate the column materials and otherwise dispose of the recovered arsenic.

Other modifications and advantages of the present invention will be apparent to those skilled in the art, without departing from the scope of this invention which is to be construed only by reference to the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for treating arsenic-containing water intended for drinking purposes comprising adjusting pH of said arsenic-containing water to the range 4-8.3, and treating said water with ferric ions to precipitate ferric arsenate therefrom and thus produce drinking water containing below 0.05 ppm arsenic.

2. A process as claimed in claim 1 wherein said water is treated with ferric hydroxide.

3. A process as claimed in claim 2 wherein said ferric hydroxide is deposited on a porous support material.

4. A process as claimed in claim 3 wherein said porous support material is a finely divided inorganic material selected from the group comprising: scheelite, kieselguhr, vermicullite, fullers earth, alumina, diatomite and montmorillonite.

5. A process as claimed in claim 3 wherein said porous support material is a molecular sieve.

6. A process as claimed in claim 2, 3 or 4 wherein the pH is in the range 4.4-4.7.

7. A process as claimed in claim 3, 4 or 5 wherein said ferric hydroxide is produced in situ on said porous support material.

8. A process as claimed in claim 3, 4 or 5 wherein said porous support material is impregnated with an aqueous solution of a water soluble ferric salt and ferric hydroxide is precipitated therefrom by addition of a sufficient quantity of a base.

9. A process for removing a substantial proportion of arsenic from water for drinking purposes comprising passing said water, at a pH in the range 4-8.3, through a bed of a porous support material having impregnated thereon ferric hydroxide.

10. A process as claimed in claim 9 wherein the pH is in the range 4.4-4.7.

11. Apparatus for use in treatment of water for drinking purposes comprising means containing a bed of a porous support material having impregnated thereon ferric hydroxide.

12. Apparatus as claimed in claim 11 wherein said means comprises a cartridge means, containing a column of said porous material, having an inlet and an outlet, adapted for attachment to a water distribution system.

13. Apparatus as claimed in claim 11 or 12 wherein said porous support material comprises a finely divided inorganic material selected from the group comprising: scheelite, kieselguhr, vermicullite, fullers earth, alumina, diatomite and montmorillonite.

14. Apparatus as claimed in claim 11 or 12 wherein said porous support material is a molecular sieve.

15. A water treatment system for removing arsenic from water intended for drinking purposes comprising:

(a) water supply means;

(b) container means for attachment to said water supply means; and

(c) porous support material in said container means having impregnated thereon ferric hydroxide.

16. A system as claimed in claim 15 wherein said container means comprises a cartridge, having inlet and outlet means, containing a column of said porous support material.

17. A system as claimed in claim 15 wherein said support material is a finely divided inorganic material selected from the group comprising: scheelite, kieselguhr, vermicullite, fullers earth, alumina, diatomite and montmorillonite.

18. A system as claimed in claim 15 wherein said support material is a molecular sieve.

19. A system as claimed in claim 17 including means to control pH in a range 4-8.3.

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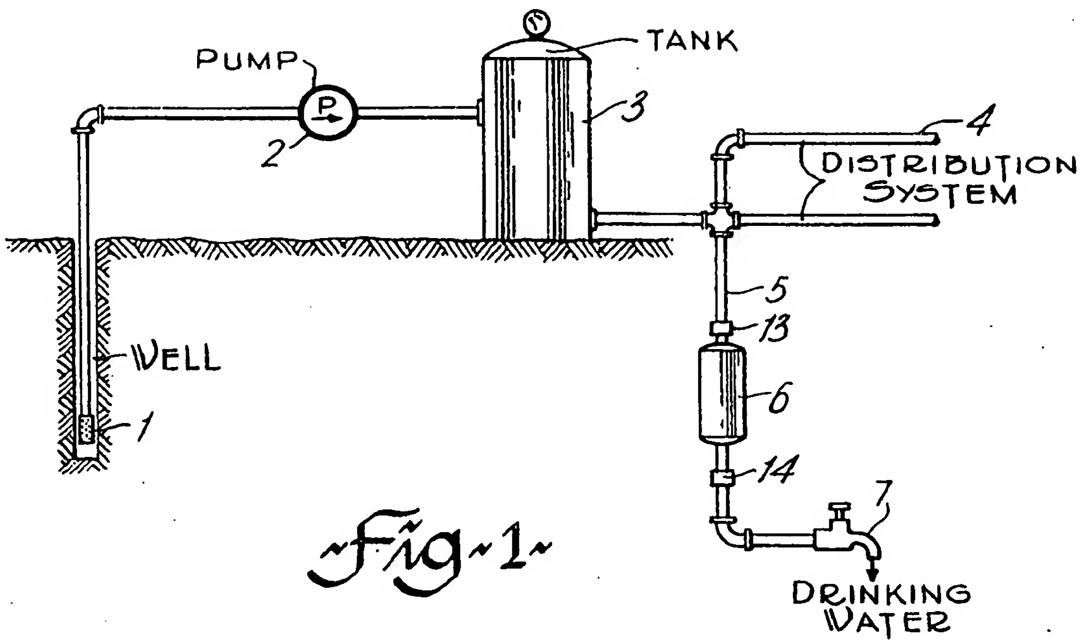
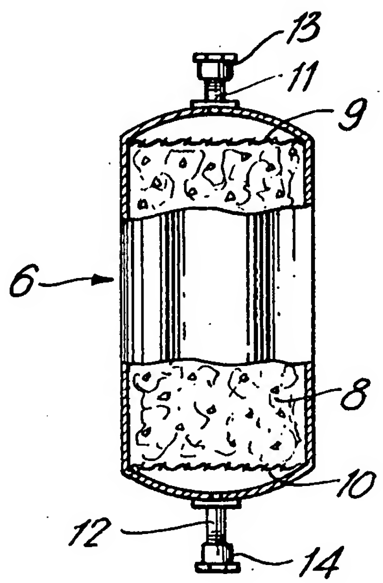


~Fig~1~



~Fig~2~